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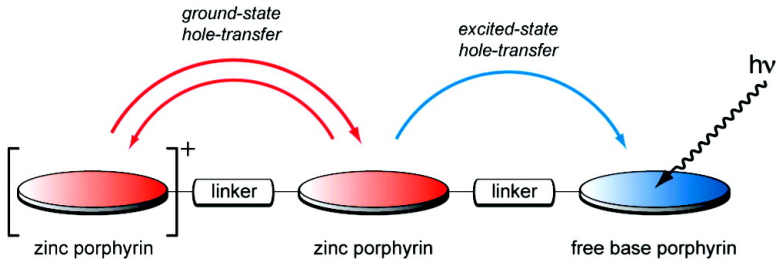

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Determination of Ground-State Hole-Transfer Rates Between Equivalent Sites in Oxidized Multiporphyrin Arrays Using Time-Resolved Optical Spectroscopy

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Abstract: Excited-state charge separation in molecular architectures has been widely explored, yet ground-state hole (or electron) transfer, particularly involving equivalent pigments, has been far less studied, and direct quantitation of the rate of transfer often has proved difficult. Prior studies of ground-state hole transfer between equivalent zinc porphyrins using electron paramagnetic resonance techniques give a lower limit of $\sim$(50 ns)$^{-1}$ on the rates. Related transient optical studies of hole transfer between inequivalent sites [zinc porphyrin (Zn) and free base porphyrin (Fb)] give an upper limit of $\sim$(20 ps)$^{-1}$. Thus, a substantial window remains for the unknown rates of ground-state hole transfer between equivalent sites. Herein, the ground-state hole-transfer processes are probed in a series of oxidized porphyrin triads (ZnZnFb) with the focus being on determination of the rates between the nominally equivalent sites (Zn/Zn). The strategy builds upon recent time-resolved optical studies of the photodynamics of dyads wherein a zinc porphyrin is electrochemically oxidized and the attached free base porphyrin is photoexcited. The resulting energy- and hole-transfer processes in the oxidized ZnFb dyads are typically complete within 100 ps of excitation. Such processes are also present in the triads and serve as a starting point for determining the rates of ground-state hole transfer between equivalent sites in the triads. The rate constant of the Zn/Zn hole transfer is found to be (0.8 ns)$^{-1}$ for diphenylethyne-linked zinc porphyrins and increases only slightly to (0.6 ns)$^{-1}$ when a shorter phenylene linker is utilized. The rate decreases slightly to (1.1 ns)$^{-1}$ when steric constraints are introduced in the diarylethyne linker. In general, the rate constants for ground-state Zn/Zn hole transfer in oxidized arrays are a factor of 40 slower than those for Zn/Fb transfer. Collectively, the findings should aid the design of next-generation molecular architectures for applications in solar-energy conversion.

I. Introduction

The design and synthesis of molecular architectures that absorb light and give long-lived charge-separated states is an essential focus in artificial photosynthesis and in the development of novel solar-energy conversion materials. Efforts to mimic the efficient processes that occur in photosynthetic reaction centers initially yielded donor−acceptor dyads and over time have given rise to arrays containing a handful of redox-active components.[1−10] Upon photoexcitation to give an initial charge-separated state in an array, the resulting unpaired electron typically undergoes stepwise transfer along a chain of acceptors; similarly, the resulting hole can undergo stepwise transfer along a chain of donors. Such subsequent transfers are ground-state processes that typically give an increasingly long-lived charge-separated state.

While studies of excited-state electron (or hole) transfer in multiporphyrin arrays have received extensive attention, ground-state hole transfer has been much less studied despite the

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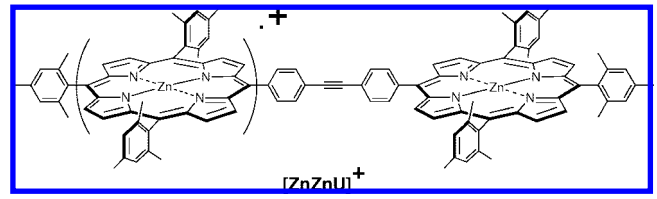
fundamental importance of this process. We note that the term "hole transfer" is used herein even though the net transport of a hole could occur via either direct hole migration or electron migration in the reverse direction. Our chief interest here is to determine the rate of ground-state hole transfer between equivalent porphyrins in multiporphyrin arrays. The motivation is 2-fold: (1) The rate of hole transfer among equivalent porphyrin constituents is of fundamental interest for understanding electronic communication[11] and provides a benchmark for comparison with hole-transfer processes among inequivalent constituents. (2) Gaining a fundamental understanding of such ground-state hole-transfer processes might allow the design of simpler synthetic reaction centers. For example, most artificial reaction centers composed of multiple constituents have been designed with an energy gradient to direct the flow of the electron and the hole.[1−10] Constructing large multicomponent architectures wherein each component is selected to give a fine thermodynamic gradient is substantially more challenging from a synthetic standpoint than the use of multiple identical components and a limited number of gradient steps to achieve the same hole−electron spatial separation. The rational consideration of the latter type of design requires knowledge of ground-state hole-transfer rates in prototypical molecular arrays. However, a chief challenge to the measurement of ground-state hole-transfer rates among equivalent constituents is the absence of signatures of the transfer process.

A number of methods have been employed to gain information about ground-state hole transfer in multicomponent architectures. Measurements of hole transport[12] are typically carried out on bulk materials in the presence of an applied field, and while relevant to the performance of materials in real-world devices, they do not provide direct information about the rate of site-to-site hole transfer. Measurements of the kinetics of charge separation and recombination in multicomponent architectures can provide rate constants for site-to-site transfer for those architectures wherein ground-state charge-shift processes follow photoinduced electron transfer, but such processes may be influenced by the Coulombic potential associated with the separated charges. This approach has been used to determine the rate of hole transfer in multiporphyrin arrays,[1−3,13] but in most if not all cases the porphyrins are not equivalent, or the transfer involves a porphyrin plus a nonporphyrin redox agent; hence, the charge shift process occurs along a thermodynamic gradient. Miyasaka et al. have employed transient absorption spectroscopy and transient dichroism measurements of polymers (e.g., poly(*N*-vinylcarbazole)) to determine hole-migration rates among the pendant aromatic moieties; in such systems, the hole is introduced by photoinduced electron transfer with a soluble electron acceptor.[14] Schanze, Miller, and co-workers studied poly(phenylene−ethynylene) bearing spectroscopically distinguishable end caps (that also serve as hole traps) and found that the rate of intrachain hole transfer to the end caps is faster ($>10^8$ s^{-1}) than bimolecular hole transfer from pulse radiolytic-generated cation radicals in solution.[15] Our groups have probed

Chart 1



ground-state hole transfer between equivalent zinc porphyrins in oxidized multiporphyrin arrays using static electron paramagnetic resonance (EPR) spectroscopy.[16,17] The EPR method does not directly measure the rate of ground-state hole transfer but rather provides a lower limit to the rate, which is set by an internal clock based on the resolution (or collapse) of the electron−nuclear hyperfine splitting.

Our earlier EPR studies of ground-state hole transfer in multiporphyrin arrays included a dyad containing equivalent zinc porphyrins ($[ZnZnU]^+$, Chart 1) as well as larger arrays containing equivalent zinc porphyrins.[16,17] For these arrays, the ground-state hole transfer is rapid on the time scale of the 4.2 MHz ^{14}N hyperfine clock, which provides an effective lower limit of $\sim(200\ ns)^{-1}$ for the hole-transfer rate between the equivalent zinc porphyrins. More recent EPR studies of ^{13}C isotopologues of $[ZnZnU]^+$ indicate that ground-state hole transfer remains rapid on the faster (~16 MHz) time scale of the ^{13}C hyperfine clock, giving a lower limit of $\sim(50\ ns)^{-1}$ for the hole-transfer rate between the equivalent zinc porphyrins.[18]

Recently, we have used transient optical spectroscopy to determine the ground-state hole-transfer rates in a series of *p,p′*-diarylethyne-linked porphyrin dyads consisting of zinc and free base porphyrins.[19] In these dyads, the zinc porphyrin is electrochemically oxidized prior to excitation of the attached free base porphyrin. One of the decay processes that re-establishes the initial state is decay of a metastable ground-state intermediate wherein the hole resides on the free base porphyrin. The ground-state hole transfer between the inequivalent free base and zinc porphyrins is downhill ($\Delta G° \approx -0.2$ eV),[17,20] and a rate of $(20\ ps)^{-1}$ is observed for the dyad analogous to ZnZnU.[19] Osuka et al. studied ground-state hole transfer between free base and zinc porphyrins and found the rate to be $(19\ ps)^{-1}$ and $(670\ ps)^{-1}$ for 1,4-phenyl and *p,p′*-biphenyl linkers, respectively.[13] In general, the rate for hole transfer between inequivalent zinc and free base porphyrins is expected to be faster than that between equivalent zinc porphyrins in arrays (e.g., ZnZnU) wherein the hole-transfer process is isoenergetic ($\Delta G° \approx 0$). However, the exact rate of hole transfer between the equivalent zinc sites in these and other arrays has not been determined. Again, the use of optical techniques to address this issue in arrays that contain a single type of redox-active pigment is not practical because the hole transfer between the equivalent zinc sites is not accompanied by a clear spectral handle.

Collectively, the prior studies of ground-state hole transfer in oxidized multiporphyrin arrays leave an extremely large window

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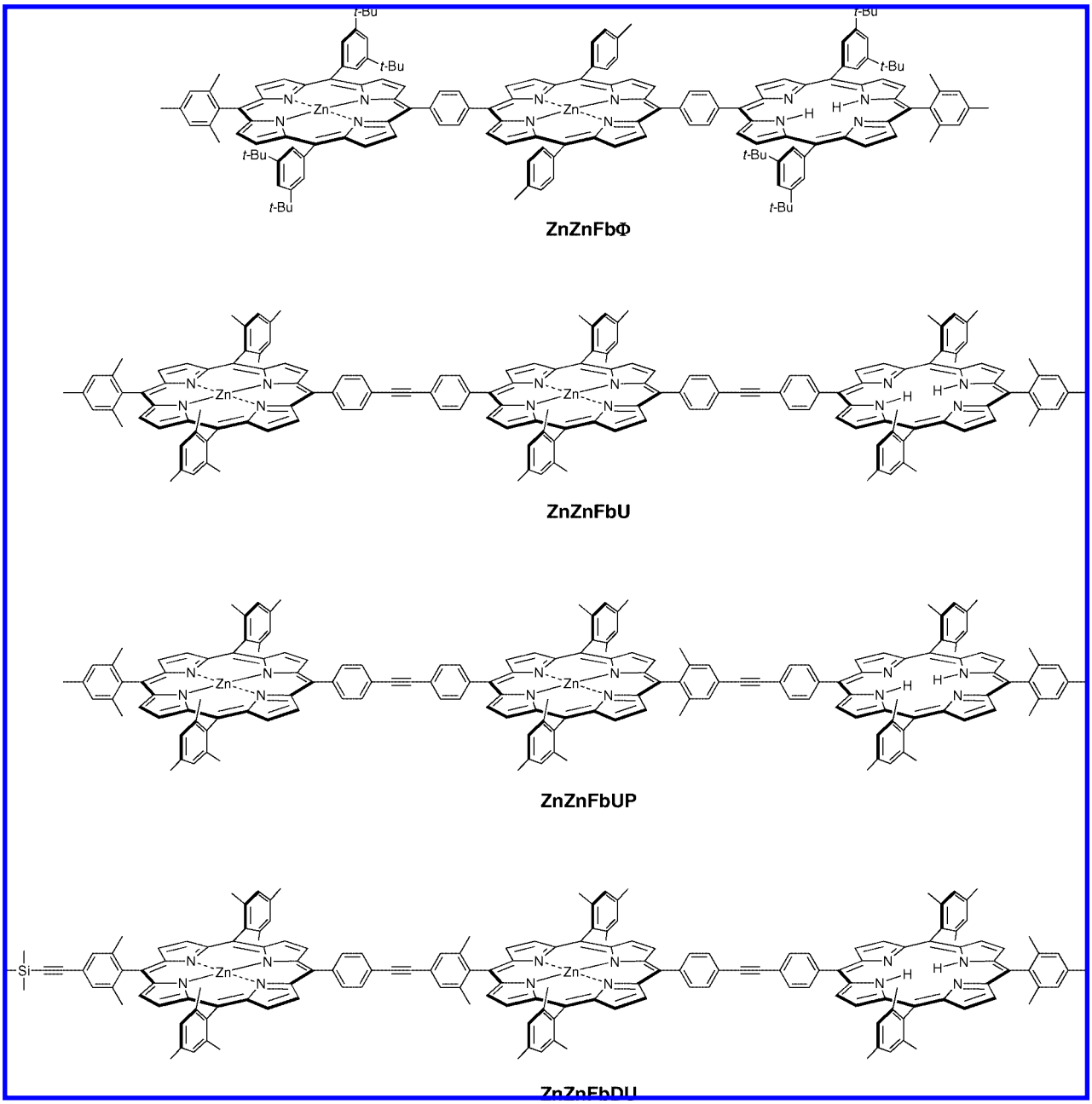
Chart 2

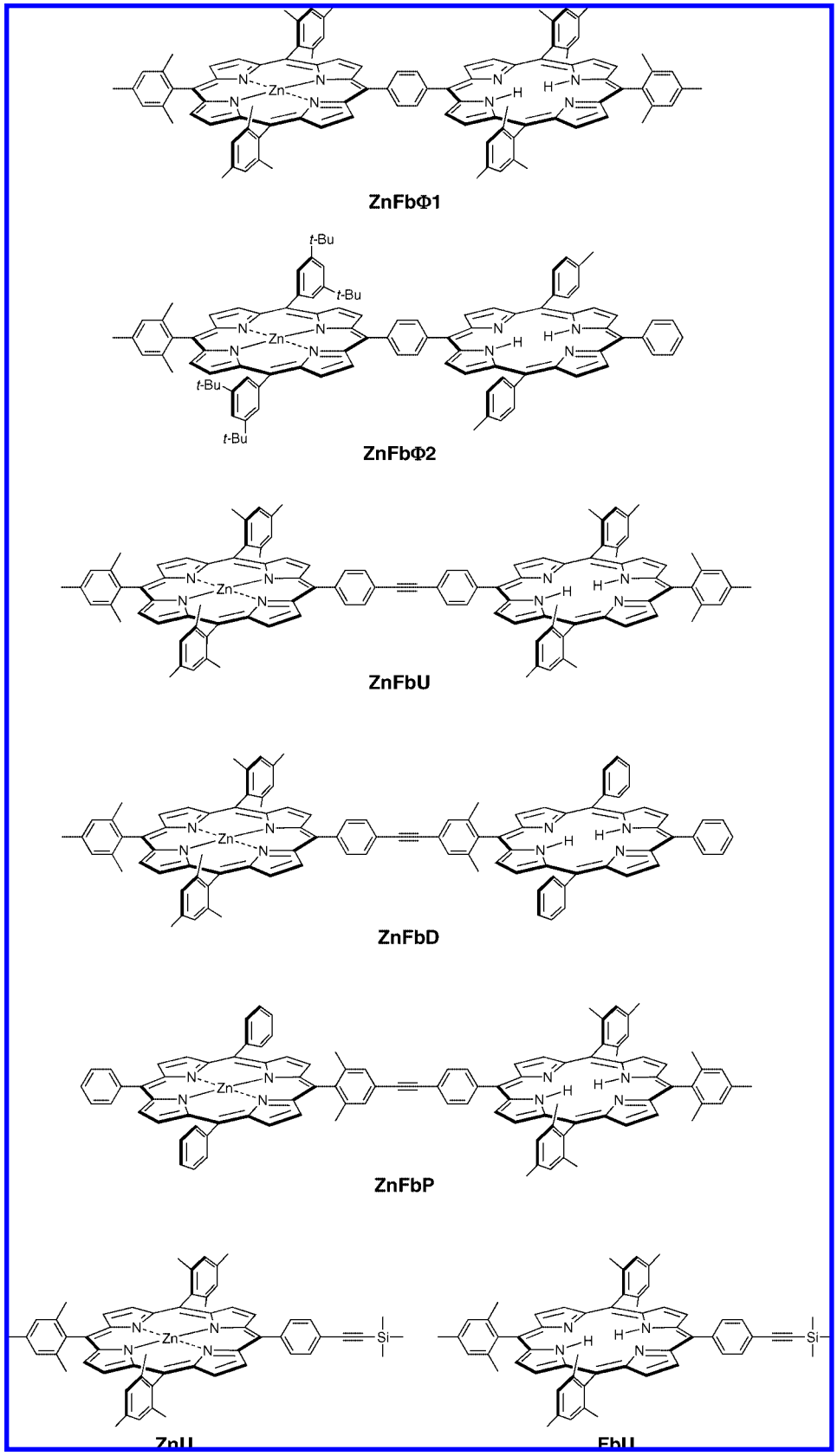


(~20 ps to ~50 ns) for the potential time scale of the process between equivalent sites. The strategy described herein utilizes time-resolved absorption studies of porphyrin triads (Chart 2) that contain two zinc porphyrins, either or both of which can be oxidized, and one free base porphyrin, which serves as a selectively excitable optical probe. In the triads, the two zinc porphyrins are not rigorously equivalent due to the nature of the molecular architecture. However, the redox potentials of the two zinc porphyrins are in fact very similar (within thermal energy at room temperature); thus, the two porphyrins are in essence equivalent with respect to the process of ground-state hole transfer. The analysis of the results is aided by our recent studies[19] on the photodynamics of analogous oxidized porphyrin dyads (Chart 3), which share many processes in common with the triads, but with the significant exception of ground-state hole transfer between two equivalent zinc porphyrins. The studies reported herein provide a definitive assessment of the rates of ground-state hole transfer between the equivalent zinc porphyrins in the various arrays. The rate constants derived from these studies should aid in the design of molecular constructs for a variety of solar-energy applications.

II. Experimental Methods

The synthesis and purification of triads [ZnZnFbU,[21] ZnZnFbDU,[22] ZnZnFbUP[21]] (Chart 2), dyads [ZnFbΦ1,[23] ZnFbΦ2,[24] ZnFbU,[21] ZnFbP,[21] ZnFbD[21]], and reference monomers [ZnU,[21] FbU[21]] (Chart 3) have been described previously. Triad ZnZnFbΦ was synthesized using established methods[24,25] as described in the Supporting Information. All studies were carried out at room temperature. Electrochemical experiments were performed under N_2 on solutions of triads, dyads, or monomers in benzonitrile (PhCN) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Studies on neutral compounds were performed in the same solvent mixture.

Chart 3



The studies utilized a three-compartment spectro-electrochemical cell modified from the original design[17] to contain an appended optical cell through which the electrolyzed solution (held at constant potential) could be flowed during the transient-absorption measurements. Further details of the measurements are given in the Supporting Information.

Static absorption spectra and fluorescence spectra (5 nm bandpass) employed deaerated (N_2 purged) solutions (1−10 μM) as

described previously.[26] Transient-absorption measurements (5−30 μM solutions in 3 mm path cells) employed ~130 fs, ~25 μJ, excitation flashes (focused to a diameter of ~1 mm) at 510 nm (oxidized arrays) or 558 nm (neutral dyads) and white-light probe pulses of comparable duration.[27] The excitation flashes were attenuated to ~8 μJ to avoid exciton annihilation.[28,29] The time evolution of the absorption difference spectra was analyzed using global analysis of the full set of kinetic profiles (to 3.9 ns) obtained by averaging ΔA in 3 nm intervals in each spectrum spanning the range 410−450 nm. The kinetic profiles were fit by the convolution of the instrument response plus a single-, double-, or triple-exponential function (e.g., $A1\cdot\exp(-t/\tau_1) + A2\cdot\exp(-t/\tau_2) + C$). Global analysis was performed using IgorPro6 (Wavemetrics); some curve fitting was performed using Origin8 (Microcal). Kinetic modeling utilized the program KINSIM[30] as discussed previously.[28,31]

III. Strategy

A. Terminology. The terms Zn, Zn*, Zn^+, or Zn^{+}* refer to the zinc porphyrin in the ground state, excited state, ground-state π-cation radical, or excited-state π-cation radical, respectively. Likewise, the terms Fb, Fb*, Fb^+, or Fb^{+}* refer to the free base porphyrin in the ground state, excited state, ground-state π-cation radical, or excited-state π-cation radical, respectively. The neutral ground states of the various dyads and triads are referred to generically as ZnFb and ZnZnFb, respectively. The oxidized and/or excited-state species use these same generic labels with the appropriate superscripts appended.

B. Overview. The objective of the present investigation is to explicitly measure the rate constant for ground-state hole transfer between the nominally equivalent zinc porphyrins in the ZnZnFb triads. The approach uses optical spectroscopic studies of the triads wherein one (or both) of the zinc porphyrins is electrochemically oxidized to the corresponding porphyrin π-cation radical (Zn^+) and the free base porphyrin is selectively excited (to give Fb*). As detailed below, photoexcitation of a free base porphyrin in an oxidized triad elicits a number of processes (including ground-state hole transfer) involving the inequivalent constituents (Zn and Fb) that are typically complete in <100 ps; the associated spectral characteristics and kinetic components for these processes have been previously well characterized in oxidized dyads and monomers (Chart 3).[19] The target ground-state hole-transfer process involving equivalent zinc-porphyrin sites in the oxidized triads is exclusive to these arrays and gives rise to a unique (longer) kinetic component that is not observed in the oxidized dyads. The approach is made more robust by comparison of the ground-state hole-transfer dynamics for (1) sets of ZnZnFb triads bearing different linkers (distance, energetic, and steric constraints) to modulate the interporphyrin electronic interactions and (2) the ZnZnFb triads in which both zinc porphyrins are oxidized prior to Fb excitation.

C. Photodynamics of Oxidized ZnFb Dyads. The strategy for probing oxidized porphyrin triads builds upon our recent study of a set of oxidized diarylethyne-linked ZnFb dyads, the most relevant of which to the present study are ZnFbU, ZnFbD, and ZnFbP (Chart 3) and for which the results are summarized below.[19] Analogous studies of phenylene-linked analogues (ZnFbΦ1 and ZnFbΦ2) are reported here for the first time because they form the basis for studies of phenylene-linked triads. The oxidized dyads (Zn^+Fb) were prepared[19] by selective oxidation of the zinc porphyrin, which is achievable because the oxidation potential for the zinc chelate is ~0.2 V less positive than that of the free base porphyrin.[20] Subsequently, the state Zn^+Fb*, produced by selective excitation[19] of the free base porphyrin, decays by parallel energy-transfer ($Zn^+Fb^* \rightarrow Zn^{+}{*}Fb$) and hole-transfer ($Zn^+Fb^* \rightarrow ZnFb^{+}{*}$) pathways (Figure 1A, solid red). Thus, the Zn^+Fb* lifetime is governed by the rate constants for both routes: $\tau_1 = [k_{ENT}^{Zn^+Fb^*} + k_{HT}^{Zn^+Fb^*}]^{-1}$. The Zn^+Fb* lifetime (τ_1) for Zn^+FbU was found to be 3.0 ps; the excited-state energy- and hole-transfer pathways were found to have comparable yields. Thus, the rate constants for Zn^+FbU are $k_{ENT}^{Zn^+Fb^*} = (6.0\ \text{ps})^{-1}$ and $k_{HT}^{Zn^+Fb^*} = (6.0\ \text{ps})^{-1}$. These values and those for Zn^+FbD and Zn^+FbP are summarized in Table 1.

For each dyad, the Zn^{+}*Fb transient state formed by the energy-transfer decay channel of Zn^+Fb* deactivates to the pre-excitation state Zn^+Fb in ≤0.5 ps, analogous to the finding of ultrafast relaxation of excited oxidized monomers (Figure 1A, dashed red).[19] Similarly, the $ZnFb^{+}$* transient state formed by the hole-transfer route relaxes in ≤0.5 ps to $ZnFb^+$, which is a metastable (ground-state) intermediate. This state for the Zn^+FbU dyad decays with a lifetime (τ_2) of 20 ps that is governed solely by the rate constant for the ground-state hole-transfer process $ZnFb^+ \rightarrow Zn^+Fb$ (Figure 1A, green). This process is thermodynamically downhill by ~0.2 eV because the zinc porphyrin is easier to oxidize than the free base porphyrin by this value.[18,20] Thus, the rate constant for ground-state hole transfer in Zn^+FbU is $k_{HT}^{ZnFb^+} = (20\ \text{ps})^{-1}$. These findings and the analogous results for Zn^+FbD and Zn^+FbP are also collected in Table 1. In summary, the photodynamics of each benchmark oxidized diarylethyne-linked porphyrin dyad (Zn^+FbU, Zn^+FbD, Zn^+FbP) have two kinetic components ($\tau_1 \approx 3-8$ ps and $\tau_2 \approx 20-40$ ps) derived from energy and hole transfer between the zinc and free base porphyrins; ultrafast relaxation of excited oxidized porphyrins also occurs but does not contribute past 1 ps.[32]

D. Anticipated Photodynamics of Oxidized Triads. Triads such as ZnZnFbU (Chart 2) can be viewed schematically as formed by appending a zinc porphyrin to a ZnFb dyad. Thus, the photodynamics of an oxidized ZnZnFbU triad should include the same processes that occur in the oxidized ZnFbU dyad, plus others that involve the second zinc porphyrin. Figure 1B shows the primary processes that can occur following Fb excitation of a generic ZnZnFb triad in which one zinc porphyrin is

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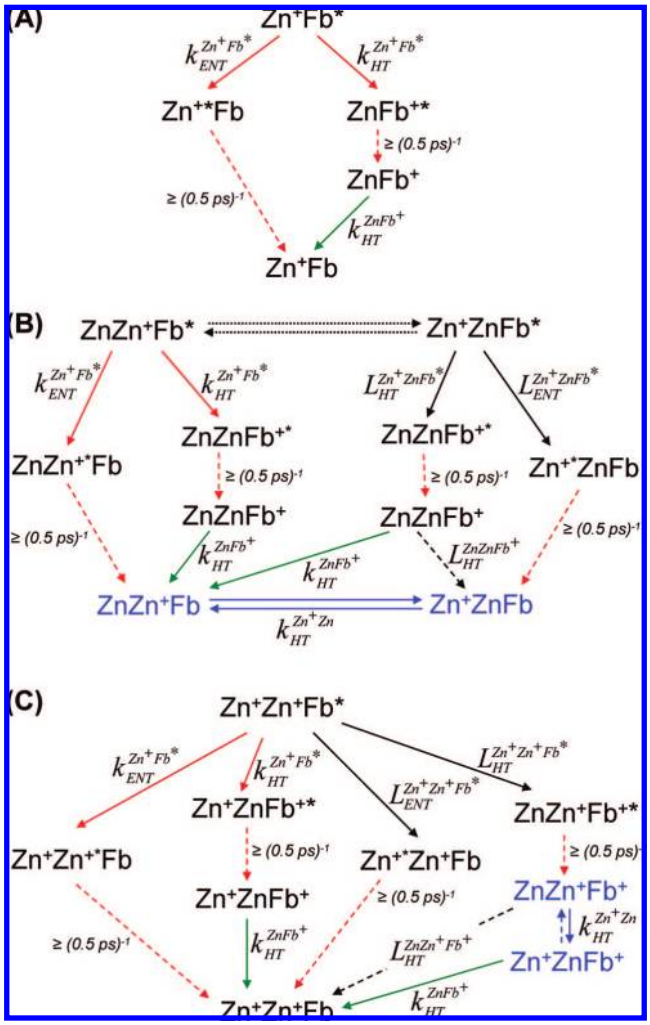

Figure 1. Kinetic schemes for (A) oxidized dyad Zn^+Fb, (B) singly oxidized triad $[ZnZn]^+Fb$, and (C) doubly oxidized triad Zn^+Zn^+Fb with diarylethyne and phenylene linkers. The solid red arrows indicate the excited-state energy- and hole-transfer processes present in the Zn^+Fb dyad; the green arrows indicate the ground-state hole-transfer process also present in the Zn^+Fb dyad; the red dashed arrows indicate the ultrafast relaxation processes measured for the oxidized monomers; the solid black arrows indicate excited-state energy- and hole-transfer processes between nonadjacent sites; the dashed black arrows indicate ground-state hole transfer between nonadjacent zinc and free base porphyrins. The states and arrows indicated in blue denote the target ground-state hole-transfer processes involving nominally equivalent adjacent sites. The rate constants for the various triads are summarized in Tables 1 and 2.

oxidized; Figure 1C illustrates the processes for a triad in which both zinc porphyrins are oxidized. For both forms of an oxidized triad, the processes described above that occur in an oxidized dyad (Figure 1A) are depicted with colored arrows: solid red for excited-state energy and hole transfer between Zn and Fb, solid green for ground-state hole transfer between Zn and Fb, and dashed red for ultrafast relaxation of an individual porphyrin that is both oxidized and electronically excited.

Below, a brief overview is given of the anticipated differences in the photodynamics of the oxidized ZnZnFb triads versus oxidized ZnFb dyads, which are key to understanding the strategy for the analysis of the results on the former arrays. The triad-specific processes not possible in the dyads are (1) energy and hole transfer involving nonadjacent Zn and Fb (Figure 2, solid arrows), for which insights can be gained from prior studies of related arrays;[28,33,34] and (2) the target ground-state hole transfer between zinc porphyrins (Figure 2, dashed arrows and Figure 1, blue).

Oxidation of one zinc porphyrin of a ZnZnFb triad produces a 50/50 ground-state mixture of Zn^+ZnFb and $ZnZn^+Fb$, and subsequent excitation of the free base porphyrin produces a 50/50 excited-state mixture of Zn^+ZnFb^* and $ZnZn^+Fb^*$ (Figure 1B). The interconversion of these two excited-state forms can be ignored because, as will be shown, this interconversion (by a ground-state hole transfer) occurs on a much longer time scale than the decay of Fb*. The Zn^+ZnFb^* and $ZnZn^+Fb^*$ excited states will then decay by parallel energy- and hole-transfer pathways. The difference in the decay routes for the two fractions is that the $ZnZn^+Fb^*$ state decays by energy- and hole-transfer process involving the adjacent zinc porphyrin, whereas Zn^+ZnFb^* decays by processes involving the nonadjacent zinc porphyrin. These processes are described in more detail below.

Decay of the $ZnZn^+Fb^*$ excited-state fraction to the $ZnZn^+Fb$ ground state (left side of Figure 1B) involves exactly the same processes that occur for the Zn^+Fb dyad (Figure 1A). Thus, in view of the results given above for oxidized dyads (Table 1), the dynamics for singly oxidized ZnZnFbU are expected to include an ~3 ps kinetic component for decay of $ZnZn^+Fb^*U$ (by parallel energy and hole transfer between adjacent Zn^+ and Fb*) and an ~20 ps component for decay of the $ZnZnFb^+U$ transient intermediate to $ZnZn^+FbU$ (by ground-state hole transfer between adjacent Zn and Fb^+).

Decay of the Zn^+ZnFb^* excited-state fraction via nonadjacent energy and hole transfer (right side of Figure 1B) is unique to the triad. These processes are denoted by black arrows with rate constants $L_{ENT}^{Zn^+ZnFb^*}$ and $L_{HT}^{Zn^+ZnFb^*}$ in Figure 1B (top right). The nonadjacent-transfer processes are illustrated schematically in Figure 2 for a generic ZnZnFb triad in which the terminal zinc porphyrin is preoxidized and the free base porphyrin is photoexcited. Our previous studies of excited-state energy and hole/electron transfer between nonadjacent porphyrins in neutral and oxidized triads and larger arrays have revealed that the rate constants are consistently a factor of 5−10 smaller than those for the analogous processes involving adjacent sites.[28,33,34] Thus, based on the observation of $\tau_1 = 3$ ps for decay of Zn^+Fb^* in Zn^+FbU (Figure 1A and Table 1),[19] the Zn^+ZnFb^* fraction of the initial excited-state mixture for singly oxidized ZnZnFbU should have a lifetime of 15−30 ps. This time scale would overlap the above-noted ~20 ps kinetics expected for decay of the intermediate $ZnZnFb^+U$ to $ZnZn^+FbU$, which occurs along the decay sequences of both initial excited-state forms (Figure 1B, green); the result would be a kinetic component with an average value of τ_2 on the order of 15−30 ps.

The key point of the above discussion is that the presence of decay channels involving nonadjacent transfers between Zn and Fb in the photodynamics of the singly oxidized ZnZnFb triads (right side of Figure 1B), like the presence of analogous processes involving adjacent Zn and Fb in the same triad (left

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Table 1. Lifetimes and Derived Rate Constants for Oxidized Dyads (Zn^+Fb)[a]

oxidized dyad	measured lifetime components			excited-state energy and hole transfer[b]		$ZnFb^+ \rightarrow Zn^+Fb$[c]
	τ_1 (ps)	ENT:HT[d]	τ_2 (ps)	$(k_{ENT}^{Zn^+Fb^*})^{-1}$ (ps)	$(k_{HT}^{Zn^+Fb^*})^{-1}$ (ps)	$(k_{HT}^{ZnFb^+})^{-1}$(ps)
$Zn^+Fb\Phi$	1.6	0.5:0.5	17	3.2	3.2	17
Zn^+FbU	3.0	0.5:0.5	20	6.0	6.0	20
Zn^+FbD	5.0	0.5:0.5	40	10	10	40
Zn^+FbP	8.0	0.4:0.6	19	20	13	19

[a] All measurements were made at room temperature in PhCN/TBAH studied under constant potential using transient absorption spectroscopy with excitation of the free base porphyrins at 510 nm. The results for all dyads except $Zn^+Fb\Phi$ are taken from ref 19, and the former are the average values for $Zn^+Fb\Phi1$ and $Zn^+Fb\Phi2$. Error in the values is 10%. [b] Rate constants for the excited-state energy-transfer (ENT) and hole-transfer (HT) decay pathways of Zn^+Fb^* determined from τ_1 and the ENT:HT ratio in columns 2 and 3. [c] The rate constant is the inverse of τ_2 because there is only one decay path. [d] Relative contributions of energy- and hole-transfer pathways to the τ_1 kinetic component determined from the global-analysis amplitude spectra at 420−425 nm as described in ref 19.

Table 2. Measured Lifetimes and Derived Average Rate Constant for Oxidized Triads[a]

Oxidized Triad	Measured Lifetime Components			Excited-State Energy and Hole Transfer				Ground-State Hole Transfer
	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)	$\left(k_{ENT}^{Zn^+Fb^*}\right)^{-1}$ (ps)[b]	$\left(k_{HT}^{Zn^+Fb^*}\right)^{-1}$ (ps)[b]	$\left(L_{ENT}^{Zn^+ZnFb^*}\right)^{-1}$ (ps)[c]	$\left(L_{HT}^{Zn^+ZnFb^*}\right)^{-1}$ (ps)[c]	$\left(k_{HT}^{Zn^+Zn}\right)^{-1}$ (ns)[d]
$[ZnZn]^+Fb\Phi$	2.3	20	0.3	4.0 ± 0.6	4.0 ± 0.6	30 ± 10	30 ± 10	0.6 ± 0.1
$Zn^+Zn^+Fb\Phi$	1.6	19	0.6					
$[ZnZn]^+FbU$	3.2	28	0.4	6.4 ± 0.3	6.4 ± 0.3	45 ± 15	45 ± 15	0.8 ± 0.1
Zn^+Zn^+FbU	2.8	18	0.9					
$[ZnZn]^+FbDU$	3.0	18	0.5	6.0 ± 0.3	6.0 ± 0.3	50 ± 20	50 ± 20	1.1 ± 0.1
Zn^+Zn^+FbDU	2.6	19	1.1					
$[ZnZn]^+FbUP$	8.0	24	0.4	20 ± 4	13 ± 3	140 ± 60	100 ± 30	0.8 ± 0.1
Zn^+Zn^+FbUP	6.8	27	0.8					

[a] All measurements were made at room temperature in PhCN/TBAH studied under constant potential using transient absorption spectroscopy with excitation of the free base porphyrins at 510 nm. The error bars are ±10% for the τ. [b] Rate constants for processes involving adjacent sites determined from τ_1 values and the branching ratios for energy transfer (ENT) and hole transfer (HT) for the corresponding dyads (Table 1). [c] Rate constants for processes between nonadjacent sites were obtained using the τ_1 values for singly and doubly oxidized forms of the triads and a reduction factor of 5−10 from the rate constants for adjacent sites in the preceding columns. [d] Average value from singly and doubly oxidized forms of the same triads.

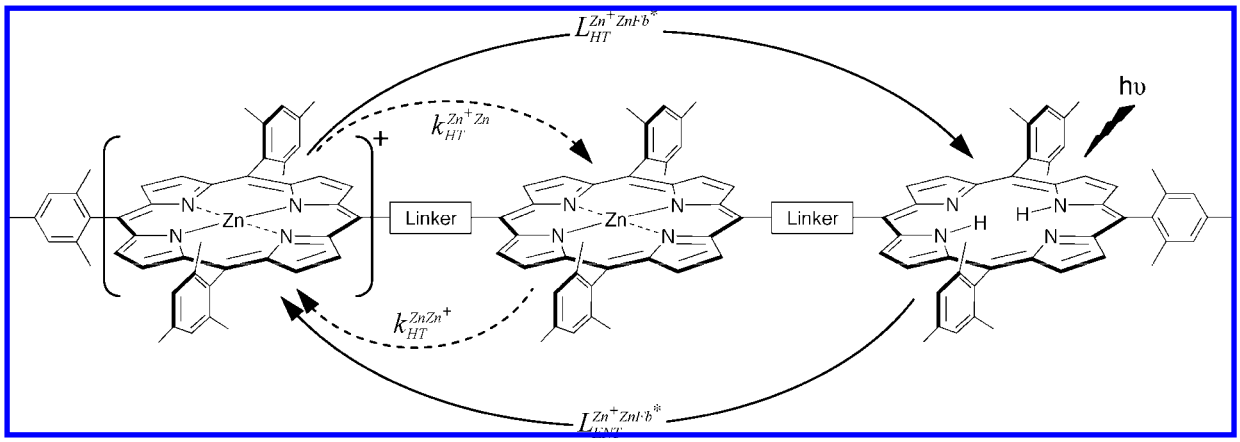

Figure 2. Energy-transfer (ENT) and hole-transfer (HT) pathways involving adjacent sites (rate constants denoted k) and nonadjacent sites (rate constants denoted L) for the singly oxidized triad Zn^+ZnFb when the free base porphyrin is excited.

side of Figure 1B) and in the oxidized ZnFb dyads (Figure 1A), will be complete by 100 ps. Moreover, any components on a time scale >100 ps in the photodynamics for a singly oxidized triad must arise from processes that do not simply involve the (adjacent or nonadjacent) zinc and free base porphyrins. The only remaining such process is ground-state hole transfer

involving the two zinc porphyrins. For a singly oxidized ZnZnFb triad, this process would involve re-establishment of the ground-state equilibrium mixture of $ZnZn^+Fb$ and Zn^+ZnFb in the same 50/50 proportion that existed prior to excitation (Figure 1B, blue). A related ground-state hole-transfer kinetic component would be expected for doubly oxidized ZnZnFb triads in which both zinc porphyrins are converted to the π-cation radical prior to Fb excitation (Figure 1C, blue).

E. Spectral Manifestations of Ground-State Hole Transfer between Equivalent Porphyrins. The final aspect of the strategy concerns a spectral signature to monitor ground-state hole transfer between the equivalent zinc porphyrins. The approach makes use of the fact that the electronic ground-state absorption spectrum of a porphyrin contains a strong near-UV Soret band ($\varepsilon > 10^5$ M^{-1} cm^{-1}) that corresponds to excitation to the second excited singlet state ($S_0 \rightarrow S_2$). In a neutral ZnFb dyad, the Soret-absorption profile is not simply the superposition of those for an equimolar mixture of the reference compounds, but differs because of the strong dipole−dipole (exciton) coupling of the Soret transitions of the zinc and free base porphyrins (Supporting Information). Thus, the two dominant Soret features of the ZnFb dyad have mixed parentage, although each feature derives more from one constituent than the other. As a consequence, the formation of the ZnFb* excited state results in bleaching in both ground-state Soret features.

Unlike the neutral ZnFb dyad, the Soret absorption feature of the oxidized dyad (Zn^+Fb) is well represented by the sum of those for the constituents. This difference in the absorption characteristics of the neutral and oxidized dyads arises because the exciton coupling of the Soret transitions of the neutral free base and oxidized zinc porphyrins is relatively weak due to the much smaller oscillator strength of the Soret transition of the zinc porphyrin π-cation radical (~410 nm) as compared to the neutral zinc porphyrin (~430 nm) (Figure 3C).[20,35] As a consequence, the formation of the Zn^+Fb* excited state results in a bleaching spectrum with one main feature due predominantly to the free base porphyrin at essentially the same position as the neutral monomer (~420 nm). These characteristics have been observed in the our recent study of oxidized (and neutral) diarylethyne-linked porphyrin dyads[19] and are illustrated by representative cases in the Results.

On the basis of the above considerations, the ground-state hole-transfer process $ZnZn^+Fb \rightarrow Zn^+ZnFb$ in an oxidized ZnZnFb triad should be accompanied by a Soret absorption-difference spectrum that nominally evolves from a single bleaching feature into two bleaching features as the constituent adjacent to the free base porphyrin evolves from Zn^+ to Zn. Thus, the key aspect in the interpretation of the kinetic data is that the triad architecture results in a unique spectral signature that allows extraction of the ground-state hole-transfer rate constant. It is important to emphasize again that although the two zinc porphyrins differ in S_2 excited-state characteristics (via differences in $S_0 \rightarrow S_2$ Soret exciton coupling with the adjacent versus nonadjacent free base porphyrin), they have effectively equivalent ground-state characteristics (because their oxidation potentials are essentially indistinguishable, vide infra).

IV. Results

A. Ground-State Redox and Optical Characteristics. The first oxidation potentials for the porphyrins in the triads and dyads in PhCN/TBAH are similar to those of monomeric porphyrins: 0.53−0.55 for zinc porphyrins and 0.70−0.80 V for free base porphyrins ($Fc/Fc^+ = 0.19$ V). This behavior is similar to that observed in other media and reflects relatively weak (but not insignificant) interporphyrin electronic coupling.[18,20,23] In this regard, it is particularly noteworthy that the oxidation of the two zinc porphyrins in a ZnZnFb triad occurs in the same reversible wave, as measured by cyclic voltammetry, and at the same peak position, as measured by square-wave voltammetry. Thus, the two porphyrins have the same potential within 20 mV, which is less than thermal energy at room temperature. Accordingly, the two zinc porphyrins of a ZnZnFb triad are effectively redox equivalent.

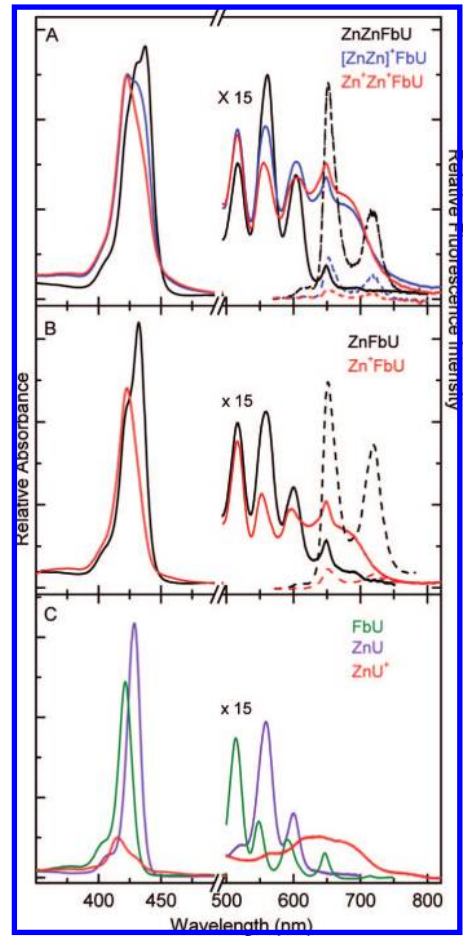

Figure 3. Absorption (solid) and fluorescence (dashed) spectra of compounds in PhCN/TBAH: (A) ZnZnFbU in its neutral form (black), one-electron oxidized form (blue), and two-electron oxidized form (red); (B) ZnFbU in its neutral (black) and oxidized (red) form; (C) neutral monomer FbU (green) and monomer ZnU in its neutral (violet) and oxidized (red) forms. The absorption spectra in the 500−820 nm region are multiplied by 15.

Bulk electrolysis of the ZnFbΦ1 and ZnFbΦ2 dyads (Chart 3) and the various diarylethyne- and phenylene-linked triads (Chart 2) produces the π-cation radical of a zinc porphyrin constituent due to its ~0.2 V less positive oxidation potential than that of a free base porphyrin.[18,20] Typically, a small (≤10%) fraction remains in the neutral form of the arrays. For the singly oxidized ZnZnFb triads, up to 20% remains in the neutral form as a consequence of the need to avoid oxidation of both zinc porphyrins (a case studied independently).

Figure 3 shows the absorbance changes that occur upon oxidation of the zinc porphyrin in ZnFbU (Figure 3B) and one

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or both zinc porphyrins in ZnZnFbU (Figure 3A). Because of the relatively weak Soret exciton coupling between the oxidized and neutral porphyrins, the absorption spectra of the oxidized dyads and triads are very similar to those for an equimolar mixture of the reference compounds (Figure 3C). Similar absorbance changes are observed for the analogous phenylene-linked dyads and triads. The prominent free base porphyrin fluorescence in the neutral ZnZnFbU triad is largely quenched upon oxidation of one or both zinc porphyrins (Figure 3A, dashed lines), as is the case for the ZnFbU dyad,[19] with the residual emission coming from the small unoxidized fraction. Similar fluorescence-quenching behavior has been observed in other porphyrin arrays upon oxidation of one constitutent.[33,34,36]

B. Photodynamics of Oxidized Phenylene-Linked ZnFb Dyads. Time-resolved spectroscopic studies were performed on $Zn^+FbΦ1$ and $Zn^+FbΦ2$ in PhCN/TBAH, which constitute a new pair of dyads relevant for understanding the photodynamics of the phenylene-linked triads. Representative transient absorption spectra and a kinetic profile with dual-exponential fit are shown in Figure 4T and N. The observations are similar to those for the diphenylethyne-linked analogue Zn^+FbU (Figure 4B and H), which have been analyzed in detail elsewhere[19] and described above (Table 1). In short, excitation of the free base porphyrin in $Zn^+FbΦ1$ or $Zn^+FbΦ2$ gives rise to two kinetic components with average values of $\tau_1 = 1.6$ ps and $\tau_2 = 17$ ps. Following the analysis for the diarylethyne-linked dyads,[19] the 1.6 ps component is assigned to decay of the initial Zn^+Fb^* excited state by parallel energy-transfer ($Zn^+Fb^* \rightarrow Zn^{+*}Fb$) and hole-transfer ($Zn^+Fb^* \rightarrow ZnFb^{+*}$) pathways (Figure 1A, solid red). The 17 ps component is attributed to the metastable state $ZnFb^+$, which decays by ground-state hole transfer to produce the Zn^+Fb initial state (Figure 1A, green).

The ratio of excited-state energy- and hole-transfer pathways of Zn^+Fb^* for each $Zn^+FbΦ$ dyad was determined to be roughly 50/50 from the global-analysis amplitude spectra (Supporting Information) via the same protocols used for Zn^+FbU and the other oxidized diarylethyne-linked dyads.[19] This result together with the average $\tau_1 = 1.6$ ps gives rate constants for the excited-state energy- and hole-transfer processes of $k_{ENT}^{Zn^+Fb^*} = (3.2\ ps)^{-1}$ and $k_{HT}^{Zn^+Fb^*} = (3.2\ ps)^{-1}$, respectively. These rate constants are about 2-fold greater than those for Zn^+FbU (Table 1). The rate constant for $ZnFb^+ \rightarrow Zn^+Fb$ ground-state hole transfer is obtained directly from the observed dynamics because it is the only process that contributes to the 17 ps lifetime (τ_2) of $ZnFb^+$. Thus, the rate constant for the ground-state hole-transfer process in the phenylene-linked dyads is the inverse of the observed lifetime, $k_{HT}^{ZnFb^+} = (17\ ps)^{-1}$. This value is only slightly greater than that for the diphenylethynyl-linked dyads, $k_{HT}^{ZnFb^+} = (20\ ps)^{-1}$.

C. Singly Oxidized Triad $[ZnZn]^+FbU$. One-electron oxidation of ZnZnFbU generates a 50/50 ground-state mixture of the states Zn^+ZnFbU and $ZnZn^+FbU$. Excitation of the free base porphyrin then generates the excited-state mixture of Zn^+ZnFb^*U and $ZnZn^+Fb^*U$ (Figure 1B). This mixture, along with $ZnZnFb^*U$ produced in a fraction of the sample that is not oxidized (see Supporting Information), is responsible for the absorbance difference spectrum at 0.5 ps after excitation (Figure 4C). The shape of this spectrum is consistent with the expectation that Zn^+ZnFb^*U (like $ZnFb^*U$ in the neutral dyad; Figure 4A) contributes two features while $ZnZn^+Fb^*U$ (like Zn^+Fb^*U in the oxidized dyad; Figure 4B) contributes one feature due to the large versus small exciton coupling of the ground-state absorption transitions of the free base porphyrin and an adjacent neutral versus oxidized zinc porphyrin.

The observation that greatly simplifies the analysis of the dynamics observed for the singly oxidized triad $[ZnZn]^+FbU$ is comparison of the time profile (Figure 4I; Table 2) with that for the oxidized dyad Zn^+FbU (Figure 4H; Table 1). The triad has three components (3.2 ps, 28 ps, 0.4 ns), whereas the dyad has two (3.0 ps, 20 ps). The similarity of the two short (τ_1 and τ_2) components for the triad and dyad and the presence of the extra longer-lived component (τ_3) for the triad can be easily understood by comparison of the associated kinetic schemes (Figure 1B versus A). As noted in the Strategy, the solid red and green arrows in Figure 1 indicate the processes that should have essentially the same rate constants in oxidized dyads and triads, and the dashed red arrows indicate ultrafast relaxation processes characterized in oxidized monomers.

The $ZnZn^+Fb^*U$ fraction of the initial excited-state mixture for the oxidized triad $[ZnZn]^+FbU$ will evolve in the same manner as in the oxidized dyad Zn^+FbU, giving rise to a $\tau_1 \approx 3.0$ ps component (decay of $ZnZn^+Fb^*U$ by parallel energy and hole transfer with rate constants $k_{ENT}^{Zn^+Fb^*}$ and $k_{HT}^{Zn^+Fb^*}$) and a $\tau_2 \approx 20-30$ ps component (decay of $ZnZnFb^+U$ with rate constant $k_{HT}^{ZnFb^+}$), as indicated on the left side of Figure 1B. [As will be seen, interconversion of $ZnZn^+Fb^*U$ and Zn^+ZnFb^*U is slow and will not contribute to the excited-state decays.] The Zn^+ZnFb^*U fraction of the initial excited-state mixture also will decay by parallel energy- and hole-transfer, but with rate constants ($L_{ENT}^{Zn^+ZnFb^*}$ and $L_{HT}^{Zn^+ZnFb^*}$) reduced (as noted above) by a factor of 5−10 because these processes involve nonadjacent rather than adjacent Zn^+ and Fb^* sites (top right side of Figure 1B, solid black). This factor results in a Zn^+ZnFb^*U lifetime of 15−30 ps (versus 3 ps for $ZnZn^+Fb^*U$). This lifetime overlaps the ∼20 ps kinetics for decay of $ZnZnFb^+U$ to $ZnZn^+FbU$ by hole transfer (Figure 1B, green) and thus only modestly shifts the net time constant of the τ_2 kinetic component in the oxidized triad (28 ps) from that in the oxidized dyad (20 ps). In this regard, these observations are consistent with the obvious expectation that the rate constant for decay of $ZnZnFb^+$ by ground-state hole transfer from Fb^+ to the nonadjacent Zn ($L_{HT}^{ZnZnFb^+}$; Figure 1B, dashed black) is much smaller than the value of $(20\ ps)^{-1}$ for the competitive, analogous process involving adjacent Fb^+ and Zn ($k_{HT}^{ZnFb^+}$; Figure 1B, green). If this were not the case, τ_2 would be shorter (not longer) than 20 ps (see Supporting Information for further analysis).

Following decay of the initial $ZnZn^+Fb^*U$ and Zn^+ZnFb^*U excited-state mixture and subsequent decay of the $ZnZnFb^+U$ intermediates by hole transfer, the states $ZnZn^+FbU$ and Zn^+ZnFbU (bottom of Figure 1B, blue) are not present in the 50/50 ratio that existed prior to excitation. Given the estimated equal branching by energy and hole transfer for both initial excited states (Zn^+ZnFb^*U and $ZnZn^+Fb^*U$), one expects a 75/25 population ratio of ground-state forms ($ZnZn^+FbU$ and Zn^+ZnFbU). These states will have different absorbance difference spectra due to the above-noted different magnitudes of exciton coupling between the Soret transitions of the free base porphyrin and the adjacent oxidized versus neutral zinc porphyrin. Thus, a spectral evolution will accompany the re-establishment of the equilibrium populations, which will occur by bidirectional $ZnZn^+ \leftrightarrows Zn^+Zn$ hole transfer between the two zinc porphyrins (bottom of Figure 1B, blue). Standard kinetic analysis of an equilibrium between two states indicates that the time evolution will have an effective time constant (τ_3) that is one-half the inverse of the (equal) rate constants for

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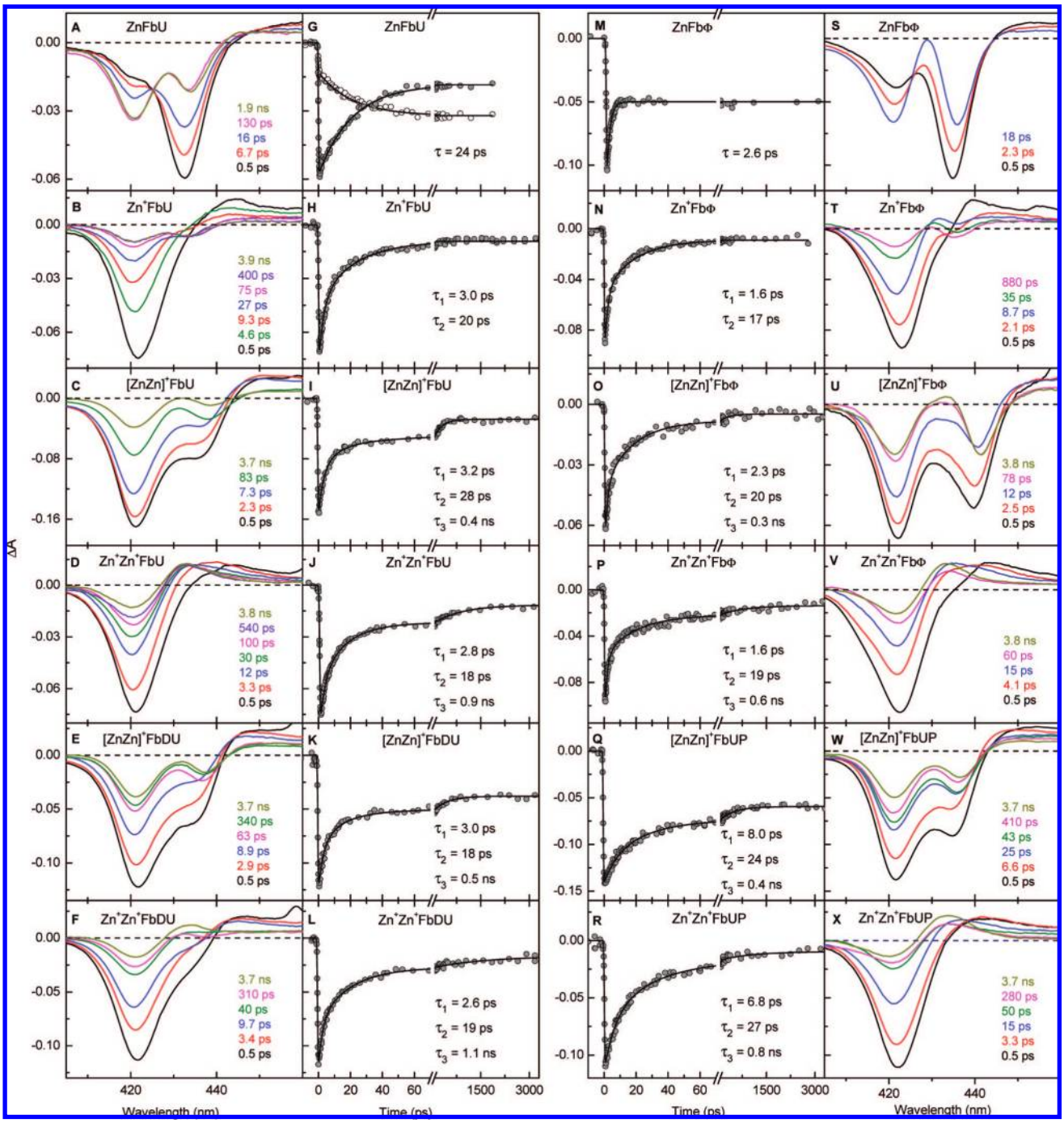

Figure 4. Transient absorption data for arrays in PhCN/TBAH at room temperature obtained using excitation with a 130 fs flash (510 nm, oxidized arrays; 558 nm, neutral arrays). Transient absorption spectra for neutral dyads ZnFb (A,S); oxidized dyads Zn^+Fb (B,T); singly oxidized triads $[ZnZn]^+$Fb (C,E,U,W); doubly oxidized triads Zn^+Zn^+Fb (D,F,V,X). Associated kinetic profiles: ZnFb (G,M); Zn^+Fb (H,N); $[ZnZn]^+$Fb (I,K,O,Q); Zn^+Zn^+Fb (J,L,P,R) using detection wavelengths of 432 nm (G; ●) and 420 nm (G; ○), 421 nm (H, J−L,Q,R), 437 nm (M), 424 nm (I,N,P), and 427 nm (O). The kinetic-profile fits utilized a function consisting of the instrument response convolved with either one, two, or three exponentials plus a constant (long-time asymptote) to give the time constants shown.

hole transfer in the forward and reverse directions. Thus, the measured time constant $\tau_3 = 0.4$ ns for $[ZnZn]^+$FbU (Figure 4I) corresponds to a hole-transfer rate constant of $k_{HT}^{Zn^+Zn} = (0.8\ ns)^{-1}$ for ground-state transfer between adjacent zinc porphyrins. This rate constant is one of the target values of this study.

D. Singly Oxidized Triad $[ZnZn]^+$FbΦ. The singly oxidized triad $[ZnZn]^+$FbΦ was examined in fashion similar to that just described for $[ZnZn]^+$FbU. A few points are worth highlighting. The absorbance difference spectra at 0.5 ps resulting from excitation of the free base porphyrin have the same two-feature bleaching (Figure 4U) as expected on the basis of the exciton-coupling arguments described above. The time profile for $[ZnZn]^+$FbΦ also has three components (2.3 ps, 20 ps, 0.3 ns; Figure 4O), whereas the Zn^+FbΦ dyad has only two (1.6 ps, 17 ps; Figure 4N). Again, the τ_1 and τ_2 components are each similar for the oxidized triad and dyad, as was found for the diphenylethyne-linked analogues (Figure 4I and H) and as is expected because the two oxidized arrays share common processes following excitation (Figure 1B and A). Using the logic given above for $[ZnZn]^+$FbU, and the τ_1 component for $[ZnZn]^+$FbΦ, the rate constants for the decay of

the initial excited states ($ZnZn^+Fb^*\Phi$ and $Zn^+ZnFb^*\Phi$) are $k_{ENT}^{Zn^+Fb^*} = k_{HT}^{Zn^+Fb^*} = (4.6\ ps)^{-1}$ and $L_{ENT}^{Zn^+ZnFb^*} = L_{HT}^{Zn^+ZnFb^*} = (35\ ps)^{-1}$. The additional $\tau_3 = 0.3$ ns component for $[ZnZn]^+Fb\Phi$, not present for $Zn^+Fb\Phi$, reflects the re-establishment of the ground-state equilibrium involving $ZnZn^+Fb$ and Zn^+ZnFb by bidirectional $ZnZn^+ \leftrightarrows Zn^+Zn$ hole transfer with a rate constant of $k_{HT}^{Zn^+Zn} = (0.6\ ns)^{-1}$. This value is only slightly larger than that of $(0.8\ ns)^{-1}$ derived above for $[ZnZn]^+FbU$ (Table 2).

E. Oxidized Triads with Steric Hindrance. Steric hindrance in the linker between zinc and free base porphyrins in oxidized ZnZnFbUP slows the excited-state dynamics (τ_1) involving these constituents as compared to the situation for ZnZnFbU (Table 2), similar to the comparison of Zn^+FbP versus Zn^+FbU (Table 1). For example, the lifetime of the $[ZnZn]^+Fb^*UP$ excited state ($\tau_1 = 8.0$ ps) is longer than that for $[ZnZn]^+Fb^*U$ (3.2 ps). On the other hand, ground-state hole transfer between zinc porphyrins is not affected. In particular, the value of $\tau_3 = 0.4$ ns for $[ZnZn]^+FbUP$ corresponding to $k_{HT}^{Zn^+Zn} = (0.8\ ns)^{-1}$ is the same as the value for $[ZnZn]^+FbU$.

The above findings for $[ZnZn]^+FbUP$ can be contrasted with those for $[ZnZn]^+FbDU$, which contains instead steric hindrance between the zinc porphyrins (Chart 2). The excited-state lifetime (τ_1) for $[ZnZn]^+Fb^*DU$ (3.0 ps) is comparable to that of $[ZnZn]^+FbU$ (3.2 ps). On the other hand, ground-state hole transfer between the zinc porphyrins is slightly slowed. In particular, the longer τ_3 value for $[ZnZn]^+FbDU$ versus $[ZnZn]^+FbU$ (0.5 ns versus 0.4 ns) corresponds to a rate constant $k_{HT}^{Zn^+Zn}$ that is reduced by 20% [$(1.0\ ns)^{-1}$ versus $(0.8\ ns)^{-1}$].

F. Doubly Oxidized Triads. Oxidation of both zinc porphyrins of ZnZnFbU, ZnZnFbUP, ZnZnFbDU, or ZnZnFbΦ to give Zn^+Zn^+FbU, Zn^+Zn^+FbUP, Zn^+Zn^+FbDU, or $Zn^+Zn^+Fb\Phi$, respectively, has consequences on the spectral and kinetic data that complement and reinforce the analysis given above for the singly oxidized forms of the triads. The photodynamics of the doubly oxidized triads is summarized below.

(1) The absorbance difference spectra at 0.5 ps for the doubly oxidized triads (Figure 4D, F, V, and X) like oxidized dyads (Figure 4B and T) have one main bleaching for the neutral free base porphyrin in contrast to the dual-featured bleaching spectra for singly oxidized triads (Figure 4C, E, U, and W) and neutral dyads (Figure 4A and S). This behavior is a further manifestation of the differential Soret exciton coupling of the neutral free base porphyrin with an adjacent neutral versus oxidized zinc porphyrin.

(2) The value of the τ_1 component for each doubly oxidized triad is smaller than that for the singly oxidized form (Figure 4 and Table 2). For example, τ_1 for Zn^+Zn^+FbU (2.8 ps) is shorter than that for $[ZnZn]^+FbU$ (3.2 ps). Inserting $k_{ENT}^{Zn^+Fb^*} = k_{HT}^{Zn^+Fb^*} = (6.4\ ps)^{-1}$ and $L_{ENT}^{Zn^+ZnFb^*} = L_{HT}^{Zn^+ZnFb^*} = (48\ ps)^{-1}$ estimated above for $[ZnZn]^+FbU$ into the kinetic scheme for Zn^+Zn^+FbU predicts a $Zn^+Zn^+Fb^*U$ lifetime of 2.8 ps, which equals the measured value (Table 2). This effect occurs because the excited state responsible for the short (τ_1) component decays by two pathways (involving only adjacent Zn^+ and Fb*) for singly oxidized triads (Figure 1B, top left) but by four pathways (involving both adjacent and nonadjacent Zn^+ and Fb*) for doubly oxidized triads (Figure 1C).

(3) The doubly oxidized triads, like the singly oxidized forms, exhibit a long (τ_3) kinetic component that is not present in the oxidized dyads and involves ground-state hole transfer between zinc porphyrins. In the simplest analysis, the τ_3 component in the kinetic profile for each doubly oxidized triad (Figure 4J, L, P, R) reflects the unidirectional ground-state hole-transfer process $ZnZn^+Fb^+ \rightarrow Zn^+ZnFb^+$ (Figure 1C, blue). Thus, the measured τ_3 values are simply the inverse of the hole-transfer rate constants. [Further information about this analysis is provided in the Supporting Information.] The $k_{HT}^{Zn^+Zn}$ values for the doubly oxidized triads Zn^+Zn^+FbU [$(0.9\ ns)^{-1}$], Zn^+Zn^+FbUP [$(0.8\ ns)^{-1}$], Zn^+Zn^+FbDU [$(1.1\ ns)^{-1}$], and $Zn^+Zn^+Fb\Phi$ [$(0.6\ ns)^{-1}$] are in good agreement with those for the singly oxidized forms $[ZnZn]^+FbU$ [$(0.8\ ns)^{-1}$], $[ZnZn]^+FbUP$ [$(0.8\ ns)^{-1}$], $[ZnZn]^+FbDU$ [$(1.0\ ns)^{-1}$], and $[ZnZn]^+Fb\Phi$ [$(0.6\ ns)^{-1}$]. The presence of an oxidized versus neutral free base porphyrin in doubly versus singly oxidized triads appears to have little effect on the rate constant for $ZnZn^+ \leftrightarrows Zn^+Zn$ hole transfer. The average rate constants for ground- and excited-state processes derived from the various measurements on the oxidized ZnZnFb triads are collected in Table 2.

V. Discussion

The study of covalently linked arrays composed of tetrapyrrole pigments has been primarily motivated by the desire to model processes of energy and charge transfer that occur in natural photosynthetic systems.[1−11,37] These studies have largely focused on either charge separation or energy transfer in neutral arrays upon photoexcitation of a tetrapyrrole component. The studies of tetrapyrrolic arrays that contain oxidized constituents are far more limited, and the time scale of processes that are unique to such arrays is poorly characterized in general. One goal of our recent studies of oxidized porphyrin dyads was to gain insight into these processes, and to form a foundation for the present study.[19] The studies reported herein were undertaken with the aim of definitively determining the rate of ground-state hole transfer between equivalent zinc porphyrins, using the oxidized triads as the simplest molecular architecture where the strategy could be implemented. The present studies show that these rates are significantly slower than the excited-state processes of energy and charge transfer and relaxation, and ground-state hole transfer between inequivalent sites. This finding has important implications for the construction of a variety of optical and/or photonic devices and materials encompassing charge separation,[1−10] hole transport,[38,39] and hole storage.[40] The present studies also provide insights into molecular design features that can be used to control hole flow. These issues are discussed in more detail below.

A. Ground-State Hole-Transfer Rates Involving Equivalent versus Inequivalent Sites. One question that arises is whether the time scale (0.6−1.1 ns) derived herein for $Zn^+Zn \rightarrow ZnZn^+$ ground-state hole transfer in phenylene- and diarylethyne-linked porphyrin arrays is generally reasonable. One means of addressing this point is to compare the rate constants ($k_{HT}^{Zn^+Zn}$) for this process (which has a $\Delta G^\circ \approx 0$) with the values ($k_{HT}^{Fb^+Zn}$) for $Fb^+Zn \rightarrow FbZn^+$ ground-state hole transfer (which has ΔG°

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≈ -0.2 eV). The rates of the latter process are $(17\ \text{ps})^{-1}$, found here for $Zn^{+}Fb\Phi$, and $(20\ \text{ps})^{-1}$, found previously[19] for $Zn^{+}FbU$ (Table 1).

The comparison of rates of ground-state hole transfer between inequivalent (Fb/Zn) and equivalent (Zn/Zn) constituents can be assessed (to a first approximation) via classical Marcus theory. The rate of electron (or hole) transfer is given by eq 1.

$$k = (4\pi^3/h^2\lambda_s k_B T)^{1/2}|V^2| \exp\{-[(\Delta G^\circ + \lambda_s)^2/4\lambda_s k_B T]\} \quad (1)$$

Here, ΔG° is the standard free energy change for the process, λ_s is the solvent reorganization energy, k_B is Boltzmann's constant, T is the absolute temperature, and V is the electronic coupling for the process.[41] The value of λ_s depends on solvent properties and the sizes and separation of the adjacent porphyrins and is estimated to be 1.4 eV for phenylene-linked porphyrins and 1.6 eV for diphenylethyne-linked porphyrins in benzonitrile (see Supporting Information).

Using eq 1 with $\Delta G^\circ \approx -0.2$ eV or $\Delta G^\circ \approx 0$ and λ_s from above gives ratios of rate constants $k_{HT}^{Fb^+Zn}/k_{HT}^{Zn^+Zn} \approx 40$ for both the diphenylethyne and the phenylene linkers. Using $k_{HT}^{Fb^+Zn} \approx (20\ \text{ps})^{-1}$ measured above predicts $k_{HT}^{Zn^+Zn} \approx (0.8\ \text{ns})^{-1}$. This predicted value is comparable to the measured values of $k_{HT}^{Zn^+Zn} = (0.8\ \text{ns})^{-1}$ for diphenylethyne-linked zinc porphyrins and $(0.6\ \text{ns})^{-1}$ for phenylene-linked zinc porphyrins. Accordingly, the observed ground-state hole-transfer rates between the equivalent and inequivalent porphyrins are generally consistent with those expected on the basis of classical (normal region) Marcus behavior.

B. Effect of Linker Length and Energetics on Ground-State Hole Transfer. A second question concerns the effects (or lack thereof) of linker length and linker energetics on the ground-state hole-transfer rates. In this regard, the ground-state hole-transfer process is mediated by through-bond electronic interactions wherein the linker serves as a super-exchange element. In the simplest picture, the tunneling probability through the linker scales (exponentially) with the product of the barrier height and width. The studies herein indicate that the rate constant for ground-state hole transfer between zinc porphyrins slows only marginally from $(0.6\ \text{ns})^{-1}$ across a phenylene linker to $(0.8\ \text{ns})^{-1}$ across a diphenylethyne linker. The rates for ground-state hole transfer between the free base and zinc porphyrins are also very similar [$(17\ \text{ps})^{-1}$ versus $(20\ \text{ps})^{-1}$] for the two types of linkers. The similarity in ground-state hole-transfer rates for the phenylene and diphenylethyne linkers suggests that the effects of distance and linker energetics largely counterbalance one another. On the one hand, the phenylene linker is shorter than the diphenylethyne linker, resulting in a narrower tunneling barrier for the former linker. On the other hand, the diphenylethyne linker has a more extended π-electron system than does the phenylene linker; thus, the relevant orbital energies (tunneling barrier height) may be lower for the former linker. The two opposing effects result in similar rates for ground-state hole transfer for the phenylene versus diphenylethyne linkers. Interestingly, the effect of changing the linker from phenylene to diphenylethyne on the rate of Zn/Fb^+ ground-state hole transfer [$(17\ \text{ps})^{-1}$ versus $(20\ \text{ps})^{-1}$] is much less than that on the rate of Zn*/Fb excited-state energy transfer in neutral dyads [$(2.6\ \text{ps})^{-1}$ versus $(24\ \text{ps})^{-1}$].[11,13,23,28,42,43] These differences in the effects of linker type on the ground- versus excited-state processes might arise because the excited states are generally more diffuse and the $\pi-\pi$ interactions between the porphyrin and the linker might therefore be more sensitive to molecular geometry. Additionally, in the superexchange formalism for the linker-mediated interporphyrin electron-exchange interaction, the linker energetics will enter in energy denominators for the porphyrin−linker−porphyrin electronic-mixing terms, which will differ for the porphyrin in the ground versus excited states.

Another factor that would be expected to contribute to the energetics of the linker-derived tunneling barrier is the presence of torsional constraints. In particular, the introduction of torsional constraints on the ortho positions of the phenyl groups of the linker would reduce the $\pi-\pi$ interactions between the porphyrin and phenyl ring, thereby increasing the tunneling barrier height and slowing the hole-transfer rates.[44] This expectation is qualitatively consistent with the observations herein. In particular, the introduction of torsional constraints on one end of the linker between the zinc porphyrins slows the Zn/Zn ground-state hole-transfer rate from $(0.8\ \text{ns})^{-1}$ in ZnZnFbU to $(1.1\ \text{ns})^{-1}$ in ZnZnFbDU. Again, the effects of torsional constraints on the rate of ground-state hole transfer are less significant than the effects of such constraints on the rates of Zn*/Fb excited-state energy transfer in neutral dyads,[11,28,42,43] and also Zn^+/Fb* excited-state energy/hole transfer in oxidized dyads (Table 1). These differences in the effects of torsional constraints on the ground- versus excited-state processes are also consistent with the view that the $\pi-\pi$ interactions between the porphyrin and the linker are more sensitive to molecular geometry in the excited versus ground state.

VI. Conclusions

Elucidating the rates of ground-state hole transfer between nominally equivalent porphyrins in molecular architectures has been the key target of this investigation. The measurement of such rates is normally difficult due to the lack of a clear spectral signature. The strategy utilized herein has been to exploit the differential exciton coupling of the $S_0 \rightarrow S_2$ (Soret) transitions of neutral−neutral versus neutral-oxidized adjacent zinc and free base porphyrins in oxidized triads (i.e., Zn^+ZnFb versus $ZnZn^+Fb$) as a means of monitoring the dynamics of ground-state hole transfer, which occurs via a linker-mediated through-bond electron-exchange interaction. The ground-state hole-transfer rates between zinc porphyrins were measured in singly and doubly oxidized triads that incorporate phenylene and diarylethyne linkers. The effect of steric hindrance in the Zn/Zn and Zn/Fb arrays also was explored. Ground-state hole transfer between equivalent porphyrins (Zn/Zn) occurs on the time scale of 0.6−1.1 ns. These values pinpoint the rate for the ground-state process, which was previously known only to be within the range of ~20 ps to ~50 ns. The Zn/Zn ground-state hole-transfer

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process is on the average 40-fold slower than Zn/Fb ground-state hole transfer, which is consistent with the different free-energy gaps for the processes ($\Delta G^\circ \approx 0$ versus $\Delta G^\circ \approx -0.2$ eV). The findings obtained herein should be useful for the design of new molecular arrays to perform simultaneous light harvesting and charge-transfer functions in solar energy-conversion systems, such as molecular-based solar cells.

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Supporting Information Available: Experimental methods; synthesis of ZnZnFbΦ; Gaussian fits for the absorption spectra of ZnFbU and ZnFbΦ; transient absorption data and kinetic schemes for the oxidized dyads and triads, and additional details on kinetic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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